

Analysis of gas-phase mercury sorption with coke and lignite dust

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Abstract. In recent years the problem of mercury emission became a widely discussed topic. Its high impact is caused by its toxicity and ability to accumulate in living organisms, properties that justified the United States Environmental Protection Agency (US EPA) to classify mercury as hazardous pollutant. The problem of mercury emission is crucial for countries like Poland, where the most of the emission is caused by coal-dependent energy sector. Current technology of mercury removal utilizes adsorption of mercury on the surface of activated carbon. Due to high price of activated carbon, this technological approach seems to be uneconomical and calls for cheaper alternative. One possible solution can be usage of other sorptive materials obtained from thermal processes like coke production. Example of such material is coke dust obtained from dry quenching of coke. The aim of this work was to analyse the sorption potential of lignite and coke dust and determine parameters influencing mercury behaviour during combustion.

1 Introduction

Prevention of mercury atmospheric emission gained a lot of popularity in recent years. Mercury is a heavy metal generally known for its toxicity, as well as high persistence in living organisms once absorbed. In spite of its trace presence in the nature, mercury and its derivatives were classified by United States Environmental Protection Agency (US EPA) as adverse for human health [1,2].

Mercury migration in natural environment is connected not only with natural sources, but also with those of anthropogenic origin. These include mainly gold mining and coal combustion processes. Coal combustion alone is responsible for annual emission of 869 Mg of Hg on global scale [3], which creates noticeable potential for emission reduction.

Poland is one of the biggest mercury emitters in Europe with emission of 10-20 Mg per annum [3,4,5], originating mostly from combustion of coal for heating and energy production. One reason of such share in emission is the energy production profile in which up to 87% of energy is produced is from subbituminous and lignite coal [6]. Another reason

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is that subbituminous coals and lignites contain from 18 – 518 $\mu\text{g Hg kg}^{-1}$ and 60 – 665 $\mu\text{g Hg kg}^{-1}$, respectively.

During combustion process Mercury can take several forms dependent on the conditions of combustion. Higher temperatures above the range of 90-120°C turn it into gaseous form Hg^0 which is the hardest to remove. If the temperature is lower, mercury becomes more reactive and it can either get absorbed by fly ash ($\text{Hg}_{(p)}$), or turn into ionic form Hg^{2+} that forms compounds with other flue gas constituents. These two forms are much easier to remove than the Hg^0 . Thus, the removal technology should incorporate influence of temperature to promote acquisition of $\text{Hg}_{(p)}$, and Hg^{2+} [10].

Studies from various pilot installations as well as those which already were included in industrial systems, hints that oxidation of mercury to its ionic form Hg^{2+} through its intermediate form $\text{Hg}_{(p)}$ is influenced by residual char and calcium in fly ashes as well as large content of halogens and sulphur in used fuel [11,12]. These studies also indicate that fuel plays key role in emissive potential of the system. Combustion of fuel with suboptimal elemental composition (small amount of Cl, Br, Fe and large content of Ca) might promote mercury migration to flue gas, instead of partial concentration in bottom ashes. This forces usage of a dedicated system segment for mercury removal to aid already functioning flue gas clean up elements, which can, but only to some extent, remove mercury passively. According to experience from US industrial plants, the most promising active technologies seems to be based on adsorption [13-16].

Among mercury removal technologies adsorption with use of activated carbon seems to be most widely used. Activated carbon is as material with developed porous structure that has proven to capture up to 90% of flue gas mercury [17]. Its main drawback is the production cost. It is estimated that cost of 90% mercury reduction varies between 66 and 220 thousand of USD per 1kg of mercury [18]. Another drawback is that activated carbon is also not fitting well to the task of mercury removal due to highly developed porous structure (as seen in table 1) that cannot be used because of relatively low concentration of mercury in flue gas. Microporous structure of activated carbon decrease the kinetic equilibrium time of adsorption process to several hours. What is more, production of activated carbon causes potential environmental problem connected with its pretreatment process [6,12,18]. This is why the technology needs more environmentally friendly and cheaper sorbents. Lignite and coke dust seems to be very promising materials for this application. Coke dust is obtained as by-product of coke dry quenching process in coking plant. Its main advantage is mesoporous structure developed without any additional treatment, decreasing production cost by several times resulting in several times with only 2.5-5 times lower volume of pores, much better kinetics of adsorption allowing for high utilization of surface and lack of environmental impact due to lack of additional pre-treatment steps.

The aim of this work was to analyse lignite coal dust and coke dust, as cheap sorbents that could substitute expensive activated carbon in flue gas mercury removal process. 10 sample mixtures of polish lignite coal and coke from pulverized coal-fired boiler localized in power plant in southern Poland were used. The mercury content of coal mixtures used in Polish energy sector were determined and the parameters influencing mercury behaviour during combustion process were identified.

2 Experimental

10 samples of lignite and coke dust mixtures were taken from pulverized coal-fired boiler from power plant located in southern Poland. The samples were homogenized and air dried until stable sample mass was achieved. Subsequently, an ultimate and proximate analysis were carried out. The ultimate analysis was performed for determination of carbon, hydrogen and sulphur content with use of ELTRA CHS – 580 apparatus, according to PN-

G-04584:2001 polish standard. Chlorine content was evaluated as a content of chlorine anions in water solution with use of direct reading spectrophotometer (DR/2000 HACH). Chlorine present in sample was transferred into liquid solution by burning a 0.5 g sample under layer of chlorine-absorbing Eschka mixture (60-72% MgO and 30-36% Na₂CO₃, POCH) mixed with sample in 1:1 weight ratio. The remaining residue was transferred to boiling deionized water and prepared for spectrophotometric analysis with use of mercuric thiocyanate (99.99%, POCH, Poland) and addition of ferric ion solution (POCH, Poland), according to PN-ISO 587:2000 standard.

For proximate analysis, humidity, volatile matter and ash content were determined with thermogravimetric analyser (ELTRA Thermostep) and calorific values of the mixtures were assayed with Leco AC 500 calorimeter, according to PN-81/G-04513 Polish standard.

All samples were additionally characterized for their ash content and sorbent materials were analyzed for their surface area. The ash content was determined by X-ray fluorescence using EDXRF spectrometer (Panalytical Epsilon 3XLE). Surface area of dusts were determined from nitrogen vapor adsorption/desorption isotherms in the temperature of 77 K with use of gas sorption analyzer using mass spectrometer (Quantachrome Instruments AUTOSORB-1-C). Before the measurement dusts were pretreated in vacuum degasser in 473 K for 12h.

The mercury concentration in samples was determined by cold vapor atomic spectrometry method (AMA 254 mercury analyzer). The method was applied for solid samples in two detection ranges (0.5-40 ng of Hg, and 40-600 ng of Hg) and detection limit of 0.01ng of mercury, allowing mercury content determination, even in trace amounts.

Sorptive potential of chosen dust materials was evaluated on laboratory scale. The 1g of fuel blend was combusted under stable air flow of 300 cm³/min and at 1123 K. The vessel with sorbent was placed at the outlet of the furnace with outlet pipe temperature stabilized with heating belt. The outlet temperature was set at either 363K or 393K. The temperature of sorbent was stabilized by thermocouple (Fig. 1).

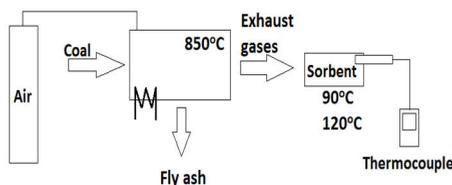


Fig. 1. Laboratory scale mercury removal measurement system for sorbent analysis

3 Results and Discussion

3.1 Sorbent comparison

Table 1 presents porous structure parameters determined from nitrogen vapor sorption/desorption isotherms in 77K. Coke dust and lignite dust are macroporous materials with lack of micropores and partial development of mesoporous structure. The total pore volume of 0.018 for coke dust is about two times smaller than that of lignite dust with its pore volume of 0.054 cm³·g⁻¹, suggesting bigger sorption capacity of a lignite. Data acquired on pore sizes also suggest that micropore/mesopore/macropore share of pore volume are 33%/50%/27% and 0%/46%/53% for coke and lignite dust, respectively. Both dust have large microporous structure. Coke dust has widely developed microporous structure and low macropore structure, while lignite dust has as much of macropore volume as mesoporous but is lacking on micropore structure. Hence, their behaviour during the experiment cannot be

Table 2. Elemental content of combusted hard coals

Sample	M ^a	V ^a	A ^a	Cl ^a	C ^a	H ^a	S ^a	Br ^a	q _{v,gr} ^a	Hg ^a
	[% m/m]							[ppm]	[kJ·kg ⁻¹]	[μg·kg ⁻¹]
W5	4.6	26.28	24.0	0.31	57.1	3.94	1.14	12.3	22.8	120.4
W6	5.4	28.20	17.7	0.33	61.5	4.35	1.23	11.8	24.4	132.2

judged on pore volume alone. Nevertheless, volume of mesopores plays a key role in their suitability as a sorbent. Mesoporous structure is important factor for sorption of large molecules, like heavy metals and has deciding role in efficiency and kinetics of adsorption in case of particles. It is also important to mention that despite lower total pore volume of coke dust it has up to 5-10 times bigger specific surface than lignite dust. Pore volume and capacity share of both dusts are also several times smaller than that of activated carbons.

Lignite and coke derived dusts are substitutes of commercial activated carbons with several times lower costs and significantly smaller impact on environment on their production stage as they don't need any additional treatment steps. Due to presence of various factors that influence mercury removal, several additional analysis was performed on waste dust in order to evaluate its potential as sorbent.

Table 1. Parameters of porous structure for analyzed sorbents, based on nitrogen vapor sorption/desorption isotherms measured in 77K.

Sample	S _{BET} [m ² g ⁻¹]	V _{DR} [cm ³ g ⁻¹]	V _{BJH} [cm ³ g ⁻¹]	V _{total} [cm ³ g ⁻¹]	S _{Hg} [mg g ⁻¹]
Coke dust (unsorted)	16,5 (16.5-32,0)	0.006	0.009	0.018	0.110-0.129
Lignite dust	3.5	0.001	0.025	0.054	0.279
Activated carbon dust	670.5	0.307	0.055	-	24.052

S_{Hg} –mercury sorption capacity, presented as [mg/g],

S_{BET} – specific surface based on Brunauer-Emmet-Teller method,

V_{DR} – micropore volume based on Dubinin-Raduszkiewicz method,

V_{BJH} – mesopore volume based on Barret-Joyner-Halenda method,

V_{total} – total pore volume.

As coal combustion-based atmospheric mercury emission is mostly influenced by mercury content in burned fuel alongside with its elemental composition, mainly sulphur, chlorine, bromine, calcium and iron content. Table 2 presents results of elemental analysis of fuel blend samples used in the experiment, along with average concentrations of mercury and chlorine. The elemental composition shows relatively similar carbon and hydrogen content between analyzed coal blends, with average carbon content of 59% with 4% of difference between blends and average hydrogen content of 4,1% with deviation below 0.4%. Most of other basic parameters is also comparable with slight difference in ash content that ranges from 24 for W5 blend to 17.7 for W6 blend. The most important parameter – the fuel mercury content ranges between 120 and 132 μg·kg⁻¹. The average concentration of chlorine, the agent partially responsible for mercury oxidation promotion, equaled up to 0.3% with concentration of other promoting agents, bromine and sulphur of around 12ppm and 1.2%, respectively.

Low concentration of promoting agents like Cl and Br, resulted in increased production of gaseous mercury Hg⁰ instead of easier to remove Hg_(p) or oxidized mercury Hg²⁺ [15]. This confirms the need for utilization of an active method in mercury removal.

The ash content of fuel blends was also evaluated (Table 3). Both sample dust and blends have typical content for hard coals with high concentration of aluminium and silicon oxides and relatively low content of other compounds. Although general composition of fuel blends has low concentration of chlorine, the elevated amount of iron (<7%), and low amount of calcium (>3%), might promote oxydation of mercury along with scarce amount of chlorine, as their individual impact on the process is not fully understood.

Table 3. Metallic content of ashes for fuel and sorbents

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	SO ₃	MnO	TiO ₂
	[%m/m]										
W5	52.29	28.71	6.85	3.16	2.32	2.79	0.86	0.41	1.45	0.08	1.01
Coke dust	42.46	28.74	9.69	6.73	2.49	2.81	1.23	1.61	2.50	0.15	1.35
Lignite dust	26.34	4.00	27.15	20.10	5.90	0.20	0.15	0.01	15.77	0.24	0.21

The characteristics of sorbents analyzed during the experiment were presented in Table 4. The best sorbent, given its purpose of atmospheric mercury emission reductor, should contain as low content of mercury and calcium, large content of chlorine, bromine, and iron. Lignite dust has mercury content of about 73.4 µg·kg⁻¹. Coke dust contains around seven times less mercury than lignite dust, four times more chlorine and two times more sulphur than the lignite dust, suggesting it is more suitable for the application as a mercury adsorbent. What is more, it also contains three times less calcium than lignite dust. However, lignite dust contains noticeably higher amount of iron, as shown in Table 3.

Table 4. Results of sorbent ultimate analysis

Sample		M ^a	V ^a	A ^a	Cl ^a	C ^a	H ^a	S ^a	q _{v,gr} ^a	Hg ^a	
		[%m/m]							[kJ·kg ⁻¹]	[µg·kg ⁻¹]	
Lignite dust		8.0	49.39	5.2	0.05	58.4	5.25	0.54	22.7	73.4	
Coke dust	Grain size [mm]	0.4	3.19	9.8	0.2	85.0	0.16	0.59	29.3	10.5	
	Y [%]										
	unsorted	-									
	x>0.2	39.6	1.3	5.1	12.0	-	79.8	-	0.65	27.8	11.2
	x<0.2	34.3	2.6	6.7	17.7	-	75.1	-	1.02	26.2	12.1
0.63>x>0.05	2.4	1.6	7.1	17.8	-	73.4	-	1.05	25.7	14.8	

The scheme of dust sorbent testing system for mercury removal in combustion processes was presented in Figure 1. The system utilizes combustion of 0.5g fuel blend in controlled conditions at 1123K, constant air flow of 300 cm³/min and exhaust gases temperature, regulated to match industrial conditions of flue gas approaching and leaving electrostatic precipitator, defined as 363K and 393K for this experiment, respectively. Results of sorbent evaluation was presented in Table 5. Efficiency of mercury removal using given sorbent was calculated according to formula (1) :

$$\eta = \frac{S_z - S_g}{C - A} \cdot 100\% \quad (1)$$

Where:

C - mass of mercury in fuel,
 S_S - mass of mercury in sorbent before analysis,
 S_Z - mass of mercury in sorbent after analysis,
 A - mass of mercury in ash.

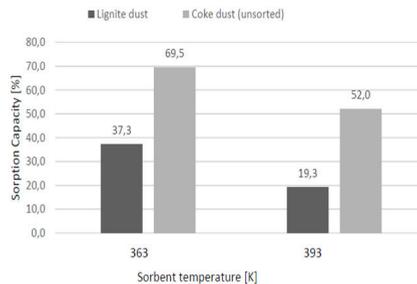


Fig. 2. Influence of sorbent temperature on Hg sorption

Based on data presented in Table 5 higher flue gas mercury sorption was achieved for coke dust, despite lignite coal having up to 2 times higher sorption capacity. Mercury take up for coke dust sorbent kept in 393K was on average around threefold higher than that of lignite coal. It may be caused by the fact that coke dust with its less developed mesoporous structure may saturate faster than lignite dust. On the other hand, lignite dust required longer time of contact with flue gas to reach its adsorption equilibrium, leading to lower overall sorption.

Both sorbents confirmed the impact of flue gas temperature on removal efficiency as much higher mercury take up was achieved in lower temperature of 363K. This phenomenon can be explained by increased Hg^0 content in higher temperature of 393K. This result suggest that mercury sorption from perspective of higher efficiency should be located after electrostatic precipitator, where flue gas temperature can be lowered to mentioned 363K. However, this setup is charged with additional cost of addition surplus gas particulate matter removal unit dedicated for sorbent dust flue gas cleanup. In case of mounting the injection system in higher temperature, the problem would be solved by presence of electrostatic precipitator after sorbent injection point. In this variant coke dust sorbent managed to remove around 52% of flue gas mercury when flue gas temperature was kept at 393K. Coke dust was also better than lignite dust, giving sorption efficiency over two times higher than lignite with sorption efficiency of around 19.3 %. Figure 3 presents simplified distribution balance of mercury during W5 fuel blend combustion. The scheme assumes that all mercury transferred from fuel to flue with exception of 0.5% that absorbed by bottom ash. During mercury sorption kept at temperature of 363K, up to 80% of mercury was emitted with flue gas to the

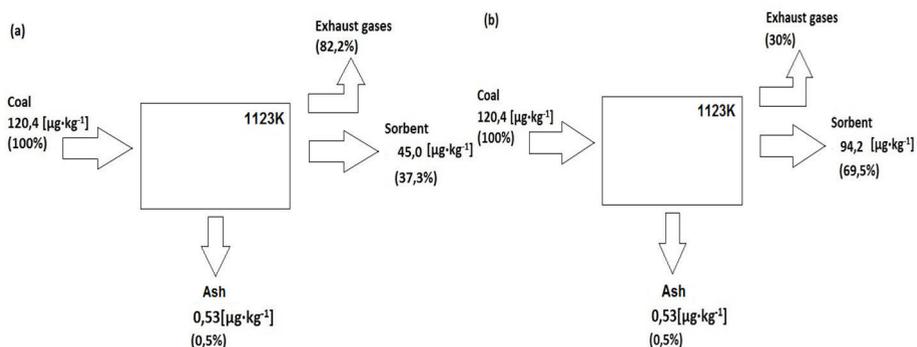


Fig. 3. Simplified distribution balance of Hg during combustion process with (a) lignite dust (b) coke dust

atmosphere (Fig 3a). With use of coke dust sorption in the same conditions the atmospheric emission of mercury was reduced to 30% (Fig. 3b).

Table 5. Amount of mercury adsorbed by dust during coal mixtures combustion

Sample	ST [K]	Coke dust (unsorted) [$\mu\text{g}\cdot\text{kg}^{-1}$]	Lignite Dust [$\mu\text{g}\cdot\text{kg}^{-1}$]
W5	363	83.7	44.9
W5	393	77.9	23.3
W6	363	62.7	44.3
W6	393	58.9	20.7

3.2 Influence of grain size on sorption efficiency

Among factors that can influence efficiency of surface-based processes like adsorption, grain size seems to be one of most important, where sorption ability of given material should decrease with its grain diameter (Fig. 4). Therefore, influence of grain diameter was also tested for Coke dust, as it seemed more promising material than the lignite dust. Unsorted coke dust was ground and sieved into three fractions: above 0.2mm; under 0.2mm, and between 0.063mm and 0.05mm. Dust with smallest diameter size gave the best result with 1.5 times higher efficiency than that of unsorted dust, which is in agreement with expected dependency. This fraction of dust achieved almost 100% of mercury removal efficiency. It must be noted that the production cost of this dust increased, which was caused by higher energy output needed and material loss connected with small size dust. The efficiency of mercury removal for other fractions was considerable (Table 4).

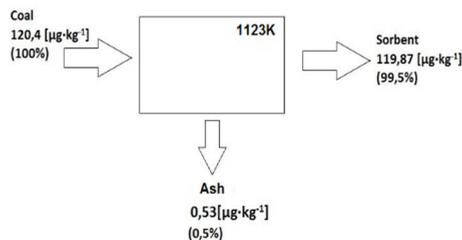


Fig. 4. Simplified distribution balance of mercury during coke dust combustion process with grain diameter between 0.065 and 0.05 mm

4 Conclusions

The aim of this study was to analyze two blends of coals combusted in polish energetic sector. The average mercury content in these blends was $126.3 \mu\text{g}\cdot\text{kg}^{-1}$. Content of other elements important for mercury removal was as follows : chlorine (0.3%) bromine (12 ppm), iron (6.8%) and calcium (2.6%).

From the perspective of optimization of mercury removal, waste dusts seem to be a better choice due to their lower cost of production. Among two tested materials, lignite dust and coke dust, the latter turned out to be better in several aspects. In comparison with lignite it possess twice as much sulphur, four times more chlorine and three times less calcium. Moreover its is 33% more efficient in mercury removal. Coke dust kept at 363K adsorbed up to $83.7 \mu\text{g}\cdot\text{kg}^{-1}$ of mercury, and up to $62.7 \mu\text{g}\cdot\text{kg}^{-1}$ of mercury at 393K. For lignite dust those results were much lower and equaled up to 44.9 at 363K and $23.3 \mu\text{g}\cdot\text{kg}^{-1}$ at 393K.

Higher removal efficiency for dust in lower temperature suggest that their injection unit should be placed farther into the cleanup system, possibly after electrostatic precipitator.

However, considering economical aspects mercury removal efficiency in higher temperature is still satisfying and allows for dust capture along with other particles in flue gases without any additional investments.

The best material was also reviewed for rain size mercury removal influence evaluation. Coke dust was also analyzed for influence of grain size on mercury removal efficiency. Grain fractions included : above 0.2mm, under 0.2mm and fraction between 0.063mm and 0.05mm. The coke dust with the lowest diameter managed to adsorb 99.6% of flue gas mercury which confirmed that additional material pretreatment allows for efficiency improvement. In contrast, the highest diameter size fraction removed only 69.7% of mercury. Optimal size fraction (in economical terms) was fraction under 0.2mm as its removal efficiency exceeded 80% with relatively low energy input required for receiving desired diameter size.

The important merit of waste dust fixed bed adsorption is much lower cost of cleanup process in comparison with commercial dust sorbents. The cost of mercury removal is set around 40-90 thousand USD per kg of mercury, while it should not be higher than 3 000 USD in commercial use [18]. Sorbents that were used in presented study were confirmed to be a good alternative to currently used activated carbon, and have noticeable potential for use in Polish energy sector. Results of presented laboratory scale experiment allow for establishing a new method for flue gas mercury removal in hard coal-based boilers.

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